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# **Luminescence Investigation of SiO<sub>2</sub> Surfaces Damaged by 0.35 mm Laser Illumination**

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## **ABSTRACT**

Following initiation at absorbing surface flaws, UV laser-induced damage to polished fused-silica surfaces continues to grow upon subsequent illumination. In this study photoluminescence spectroscopy was used to detect the formation of a modified, absorbing layer of silica that could be responsible for the continued growth of the damage site. For damage sites created with pulsed 355 nm illumination, three characteristic photoluminescence peaks are detected within the damage sites when excited with a 351 nm CW beam. Two of the peaks are likely due to the well-known E' and NBOHC defects associated with oxygen vacancies and broken Si-O bonds, respectively. The third, and dominant, peak at 560 nm has not been clearly identified, but is likely associated with a change in stoichiometry of the silica. The relative intensities of the peaks are non-uniform across individual damage sites. The photoluminescence data is being combined with insights from various optical and electron microscopies to develop an understanding of laser-induced damage sites. The objective is to develop strategies to slow or stop the growth of the damage sites.

## **1. INTRODUCTION**

The functional lifetime of fused silica components on high-power laser systems is determined by the obscuration loss resulting from laser-induced damage to the surfaces. The obscuration is the result of two processes: initiation of damage at an absorbing surface flaw, followed by growth of the damage upon subsequent illumination.[1] Through studies of polishing contamination and subsurface damage, significant progress has been made in minimizing the concentration of damage initiation sites on polished silica surfaces. At present defect densities of 1 per 100cm<sup>2</sup>, however, there would still be several damage sites on large optics such as the 40 cm x 40 cm lenses used on the National Ignition Facility laser. In an effort to minimize the impact of these damage sites, we are working to understand the mechanism for damage growth and to develop processes to slow or stop the rate of growth.

In order for laser damage process to occur some absorbing species must be present to couple the laser energy into the optical surface. For the initial damage the absorbing precursors are believed to be nano- to micron-scale defects resulting from the surface finishing processes. These precursors are almost certainly removed during the formation of the initial  $\mu\text{m}$ -scale damage site. For laser damage to continue to grow on subsequent pulses another means for laser absorption in the silica is required. It has been proposed that the plasma, and subsequent thermomechanical response, resulting from the initial damage process modifies the surrounding silica to form an absorbing layer. On subsequent pulses the modified-silica layer absorbs the laser pulse leading to growth of the damage site and the creation of a new modified layer. The focus of the present work is to determine the nature of the damage-modified silica material.

Absorbing defects in silica, and the Si-O system in general, have been extensively studied using photoluminescence (PL) emission spectroscopy. Besides the interest in radiation-induced defects in silica (excimer laser, neutron, gamma-ray) [2] there is also interest in luminescent porous silica and silicon nanoparticles, as well the defects at the Si/SiO<sub>2</sub> interface in microelectronics. This body of research provides a background for identifying modifications to the silica at laser damage sites. We report here on the use of PL spectroscopy to characterize potential absorbing defects caused by 351 nm laser-induced damage to silica surfaces.

Undamaged silica exhibits a weak luminescence as a result of ionic contaminants in the bulk material. There is no indication, however, that these contaminants play a role in the laser damage process. In general, no change in the PL of silica has been reported for non-damaging fluences of photon energies below 4.5 eV. (The only exception to this is for illumination in a vacuum environment as will be discussed below). At these low energies a higher than two-photon absorption process is required to exceed the silica bandgap. [3] In this study the change in the PL spectra are the result of the plasma created during the damage process, rather than of the 355 nm illumination directly.

## 2. EXPERIMENTAL DETAILS

The 2" diameter silica substrates used in the study were Corning 7940 or 7980 material polished at commercial vendors using processes optimized for high fluence laser applications.

Laser damage sites were created using the 355 nm beam from a tripled Nd-YAG laser. The pulse length is 7.5 ns and the beam profile is near-Gaussian with a  $1/e^2$  diameter of 1.1 mm at the sample plane. Damage sites were created on the optic using 40 J/cm<sup>2</sup> pulses and grown using additional pulses at fluences at or below this level.

The local PL spectra from the optic surface was measured using a 351 nm illumination from a CW Ar-ion laser as the excitation source and a single grating spectrometer equipped with a CCD array camera to record the emission spectra. The experimental system is shown schematically in Figure 1. The lens/pinhole combination provides confocal spectral imaging capabilities with lateral spatial resolution of ~5  $\mu$ m and depth resolution of ~10  $\mu$ m.

## 3. RESULTS

When excited at 351 nm the emission from the non-damaged surface has a peak near 520 nm, as shown in Figure 2. This emission spectrum appears the same as that measured in the bulk material although surface emission is distinctly more intense than that of the bulk. The intensity of this emission decreases as the sample is exposed to prolonged irradiation to the 351-nm CW laser beam or to 355-nm pulses and stabilizes to a level of ~20% of its original value.

An optical micrograph of a damage site resulting from 5 pulses at 40 J/cm<sup>2</sup> is shown in Figure 3. Creation of the damage site resulted in a change in the emission spectra, as well as a general increase in intensity, as shown in Figure 2. Figure 4 shows the spectra measured at five locations within the damage site. Both the total intensity and the relative intensity of individual peaks varied significantly across the damage site. In spite of the variation in the local spectral intensities, three prominent emission peaks at 440 nm, 560 nm, and 650 nm are indicated. The 560 nm is generally the dominant peak.

Additional damage sites created using varying fluences and number of pulses were also examined. The size of the damage increased with both fluence and number of pulses. The same three PL peaks were always indicated. Because there was significant variation in the magnitude of the spectra across the damage sites it was not clear whether the absolute intensity of emission varied with illumination history.

The non-uniformity of the PL spectra across the damage sites was also examined using a PL imaging system. [4] Attempts to correlate the luminescence with topographical features measured within the damage sites using SEM microscopy suggest that higher intensity luminescence may correspond with steep topographical features. It is highly likely that scattering within the complex damage morphology influences the local PL intensity. No correlation of the relative intensities of the three PL peaks with topography has yet been indicated however.

## 4. DISCUSSION

The luminescence peaks at 440 nm and 650 nm are almost certainly attributed to two well-known defects in SiO<sub>2</sub>. [5] The 440 nm peak is attributed to the E' center which is a charged oxygen vacancy. The 650 nm peak is due to the non-bridging oxygen hole center (NBOHC) which is essentially a broken Si-O bond. Both of these defects can

result from radiation damage (neutrons, gamma rays or deep UV (<300nm) illumination [2]) or from mechanical stress or damage to the material [5]. For the case of 351 nm laser damage, the defects are assumed to result the plasma created at the damage site rather than by absorption of the 351 nm irradiation itself. When a highly absorbing flaw in the silica is illuminated with the high fluence 355 nm pulse, temperatures of several thousand degrees result in the formation of a plasma at the damage site. The pressure wave caused by the expanding plasma causes mechanical damage to the surrounding silica resulting in point defects. The plasma spectra also has a small deep UV component that may also contribute to the formation of the E' and NBOHC defects.

The nature of the dominant peak at 560 nm is not clear. If SiO<sub>2</sub> decomposed as a result of the high temperatures associated with the damage plasma, substoichiometric SiO<sub>x</sub>, i.e. SiO<sub>x</sub> (0<x<2), would be the expected product. SiO<sub>x</sub> would provide high absorption levels that could account for continued growth of the damage sites.[6] Furthermore, at temperatures above 1100C SiO<sub>x</sub> is unstable and phase separates into SiO<sub>2</sub> and Si nanoparticles. At UV fluences of several J/cm<sup>2</sup> Si particles of greater than a few nanometers would heat to several thousand degrees resulting in laser damage growth. We have therefore looked for indications in the PL spectra of the presence of SiO<sub>x</sub> or Si-nanoparticles.

For high quality SiO<sub>x</sub> thin films a PL peak is reported which red-shifts with decreasing x [7]. We have observed such a shifting peak in silica surfaces exposed to non-damaging fluences at 351 nm while in a vacuum environment.[8] The resulting peak shifts from the visible to the near-IR with increasing illumination, consistent with a loss of oxygen from the surface. The connection of this luminescence with oxygen loss from the silica is supported by the observed reversal of the shift when the sample is illuminated in the presence of oxygen. Based on ref. [7] the peak at 560 nm observed in the damage sites would indicate a value of x near 1.5. It is unlikely, however, that the laser damage process would consistently lead to material with the same value of x, independent of location in the damage site or illumination history. The consistent peak at 560 nm is more likely associated to a discrete defect state.

A broad luminescence band with a peak at 2.0 to 2.2 eV (560 nm to 620 nm) has been observed in Si<sup>+</sup>-implanted silica [9, 10]. The PL band was correlated with a paramagnetic E'<sub>delta</sub> center observed using EPR. This center is attributed to small silicon clusters within SiO<sub>x</sub>. ESR line-shape simulations suggests the center is due to an unpaired spin delocalized over five silicon atoms. Based on radiative lifetimes, Ghislotti argues, however, that the 560 nm peak is due to silicon ladder structures (chains) rather than clusters.[11]. Small clusters of excess Si appears to be a possible explanation for the 560 nm peak observed at damage sites.

Nanocrystalline Si particles (nc-Si) can also lead to a photoluminescence signal where the emission wavelength is determined by the particle size. As a result of quantum confinement effects the luminescence wavelength of the nanocrystals decreases as the particle size decreases. [12] A peak at 560 nm would be attributed to the presence of nanoparticles of about 1.5-2 nm in diameter. As in the case of SiO<sub>x</sub>, it is unlikely that the laser damage process consistently produced the same size of nanoparticles. In order to further clarify this issue we are using high-resolution TEM cross-sectioning to more directly look for Si-nanocrystals within the damaged layer. It should be noted that amorphous Si particles will not be detected by TEM. Also, amorphous Si particles or nanocrystals larger than 3nm [13] to 8 nm do not luminesce. For Si particles larger than 8 nm, however, a strong Raman line should be visible at 520 cm<sup>-1</sup>. [9] Clearly, luminescence alone cannot fully address the Si-nanoparticle question.

The PL spectra for nc-Si shifts with particle size only for cases where recombination occurs within the particle. In cases where the recombination occurs through defect states at the Si-SiO<sub>x</sub> boundary a discrete, size-independent state near 730 nm is observed. Annealing of samples showing the E'<sub>delta</sub> band, discussed above, to 1100C results in the appearance of this 730nm peak. We have not detected a peak in this range in the laser damage sites.

While the explanations for the 560 considered above can be associated with near-surface oxygen loss, the PL peak has also been observed in bulk silica irradiated with 248 nm laser pulses. [14]. No explanation for the nature of the bulk peak was given. In measurements made at low temperatures (77K) a 560 nm peak is often attributed to self-trapped excitons (STE). The nature of the defect is not clear however. It has been associated with quasi-crystalline short-range order in the silica [15] and with an E'<sub>gamma</sub> center, which is a E' center paired with a diatomic oxygen interstitial [16]. Luminescence in this spectral region has also been attributed to carbon contamination. [17]

Based on insight gained from the photoluminescence studies as well as photothermal microscopy, x-ray photoelectron spectroscopy, and electron and optical microscopy we are developing a picture of the complex nature of the laser-induced damage sites. Figure 5 shows a schematic of a damage site showing that the damaged material is non-uniform both vertically and laterally. The damage site may nominally include three different layers: a layer with modified chemical composition, a layer of mechanically damaged material (crushed, compressed), followed by a region of extended cracks. It is not clear which forms of modified material within the damage site are responsible for continued growth. Also, the luminescence peaks may not directly indicate the dominant absorption process. Further study using chemical, structural, and optical techniques will be needed to clarify these issues.

## 5. CONCLUSION

The initiation of surface damage on polished fused silica using 351 nm laser pulses results in the formation of luminescent defects. For 351 nm excitation the luminescence spectra consists of three distinct peaks at 440nm, 560 nm and 650 nm. The relative intensities of these peaks is non-uniform across individual damage sites and shown no clear dependence on illumination history. The 440nm and 650 nm emission appear to be due to charged oxygen vacancies (E' center) and broken Si-O bonds (NBOHC). The nature of the 560 nm peak is not clear, although some form of Si excess is a likely possibility.

## 6. ACKNOWLEDGMENTS

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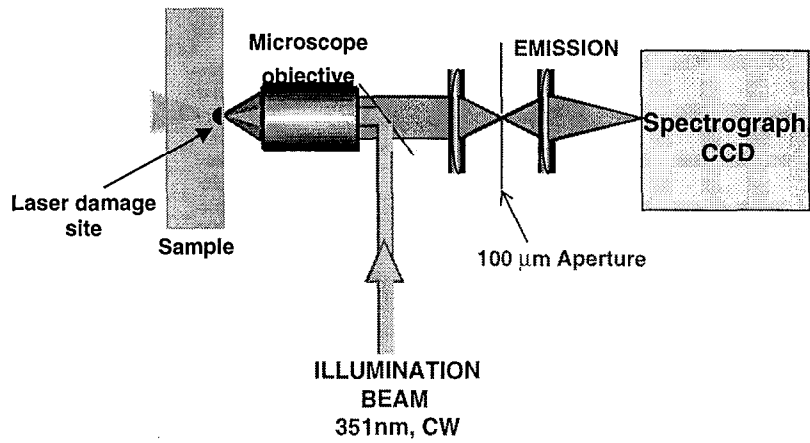


Figure 1: Schematic of photoluminescence confocal microscope used to study laser damage sites.

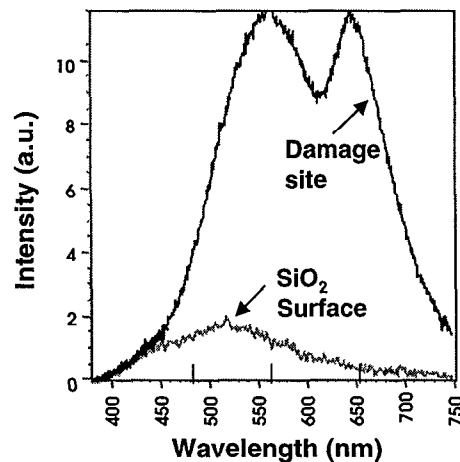


Figure 2: Photoluminescence spectra measured for non-damaged SiO<sub>2</sub> surface and within damage site shown in figure 3.

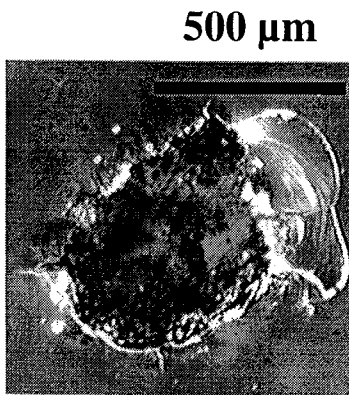


Figure 3: Optical micrograph of laser damage site initiated with a single 355 nm pulse at 40 J/cm<sup>2</sup>, 7.5 ns and growth for an additional four pulses at the same fluence.

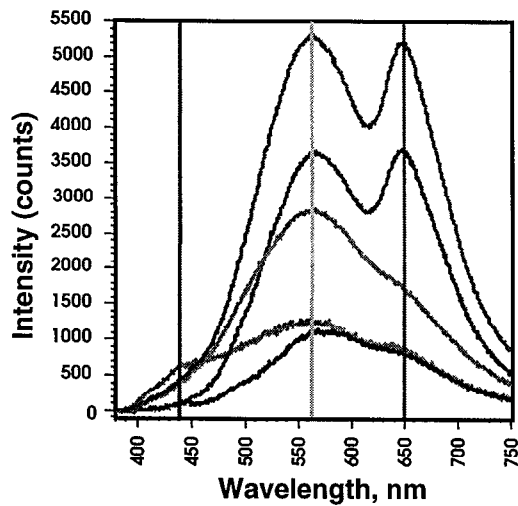


Figure 4: Photoluminescence spectra measured at several 5 mm diameter areas within the damage site shown in Figure 3.

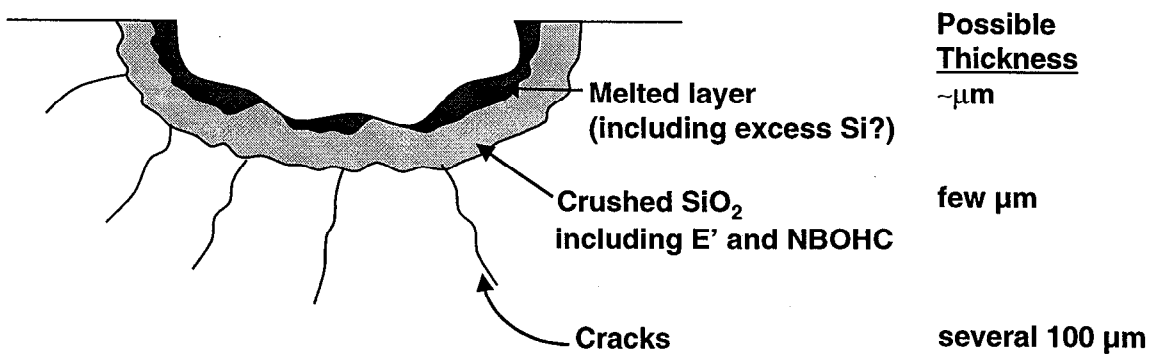


Figure 5: Schematic of potential layered structure of a silica surface modified by laser-induced damage.